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European Patent Office
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⑪ Publication number:

0 253 567
B1

⑫

EUROPEAN PATENT SPECIFICATION

- ⑯ Date of publication of the patent specification: **05.12.90**
- ⑯ Application number: **87306047.9**
- ⑯ Date of filing: **08.07.87**
- ⑮ Int. Cl. 5: **C11D 3/37, C11D 17/04**

⑭ Laundry compositions.

- ⑩ Priority: **15.07.86 GB 8617255**
- ⑬ Date of publication of application: **20.01.88 Bulletin 88/3**
- ⑮ Publication of the grant of the patent: **05.12.90 Bulletin 90/49**
- ⑯ Designated Contracting States: **AT BE CH DE FR GB GR IT LI LU NL SE**
- ⑯ References cited:
EP-A-0 001 305
EP-A-0 199 403
EP-A-0 217 186
GB-A-2 137 221
US-A-3 712 873
US-A-3 893 929
US-A-3 962 152
US-A-4 125 370

The file contains technical information submitted after the application was filed and not included in this specification

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EP O 253 567 B1

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Description**TECHNICAL FIELD**

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The present invention relates to laundry detergent compositions. In particular, it relates to laundry detergent compositions containing soil-release agents.

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In addition to cleaning, laundry detergent compositions desirably have other benefits. One is the ability to confer soil release properties to fabrics, particularly those woven from polyester fibres. These fabrics are mostly co-polymers of ethylene glycol and terephthalic acid, and are sold under a number of tradenames, e.g. Dacron (RTm), Fortrel (RTm), Kodel (RTm) and Blue C Polyester (RTm). The hydrophobic character of polyester fabrics makes their laundering difficult, particularly as regards oily soil and oily stains. The oily soil or stain preferentially "wets" the fabric. As a result, the oily soil or stain is difficult to remove in an aqueous laundering process.

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High molecular weight (e.g., 40,000 to 50,000 M.W.) polyesters containing random ethylene terephthalate/polyethylene glycol terephthalate units have been used as soil release compounds in laundry detergent compositions – see for example US-A 3 962 152 and US-A 3 959 230. During the laundering operation, these soil release polyesters adsorb onto the surface of fabrics immersed in the wash solution. The adsorbed polyester then forms a hydrophilic film which remains on the fabric after it is removed from the wash solution and dried. This film can be renewed by subsequent washing of the fabric with a detergent composition containing the soil release polyesters.

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A major disadvantage of the known detergent formulations, however, is that they can adversely affect cleaning performance in other areas of laundry detergency, especially clay soil detergency.

Presumably this is the result of the polymer depositing on soil which is already adhered to the fabric surface, thereby preventing solubilization or dispersion of the soil by other components of the detergent composition.

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It is also known that introducing specific quaternary ammonium surfactants into the aqueous laundry liquor can provide increased deposition of terephthalate-based soil-release polymers and hence provide superior removal of oily soils and stains (see US-A 4 132 680).

Quaternary ammonium surfactants are themselves known to have a detrimental effect on clay soil detergency and anti-redeposition and, if anything, therefore adding a quaternary ammonium surfactant merely compounds the problem.

US-A 3 893 929 describes the application of certain low-molecular weight terephthalate soil clean agents to textiles in an aqueous acidic rinse bath. US-A 3 712 873 relates to textile-treating compositions containing low-molecular weight terephthalate soil release agents for application to textiles by spraying or padding.

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It has now been discovered that certain terephthalate soil release polymers having a specified ratio of ethyleneoxy terephthalate to polyethyleneoxy terephthalate units and specified molecular weight and preferably having polyethyleneglycol terminating groups at both ends of the polymer chain provide excellent soil-release performance in a detergency context without detriment to clay soil detergency and anti-redeposition. Indeed in low or zero phosphate detergent compositions, clay soil cleaning performance is actually enhanced. Furthermore, incorporation of a water-soluble quaternary ammonium surfactant promotes further increases in polymer deposition and improved soil-release performance again surprisingly without detriment to clay-soil detergency. Moreover, the quaternary ammonium surfactant is beneficial from the viewpoint of promoting soil-release performance in the presence of anionic surfactant components.

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SUMMARY OF THE INVENTION

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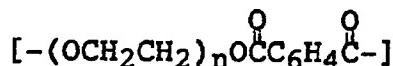
According to one aspect of the invention, therefore, there is provided a laundry detergent or detergent additive composition comprising (a) from 0.1% to 25% by weight of a soil-release polymer comprising ethyleneoxy terephthalate (EO-T) units and polyethyleneoxy terephthalate (PEO-T) units at a molar ratio (EO-T/PEO-T) of from 0.6 to 0.95, the PEO-T units containing polyethylene oxide (PEO) linking units having a molecular weight of from 300 to 3000, the molecular weight of the polymer being in the range from 900 to 9,000, (b) from 0.1% to 20% of a water-soluble quaternary ammonium surfactant, and (c) from 5% to 75% of anionic or nonionic surfactant, wherein the nonionic surfactant comprises an ethyleneoxide condensation product selected from C₈-C₂₄ primary or secondary aliphatic alcohol having from 2 to 9 moles of ethylene oxide per mole of alcohol.

The compositions of the invention contain from 0.1% to 25%, preferably from 0.2% to 15%, more preferably from 0.3% to 10%, of a soil release polymer containing ethyleneoxy terephthalate (EO-T) groups having the formula:

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5 polyethyleneoxy terephthalate (PEO-T) groups having the formula:



10 wherein the molar ratio of ethyleneoxy terephthalate to polyethyleneoxy terephthalate in the polymer is from 0.6 to 0.95. The molecular weight of the polyethylene oxide linking unit is in the range from 300 to 3,000 i.e., n in the above formula is an integer of from 7 to 70. The polymers have an average molecular weight in the range from 900 to 9,000. The polymers are also characterized by a random polymer structure, i.e., all possible combinations of ethyleneoxy terephthalate and polyethyleneoxy terephthalate can be present.

15 Highly preferred from the viewpoint of acceptable clay-soil detergency are soil-release polymers comprising at least 10%, preferably at least 20% thereof (molar basis) of components wherein both chain terminating units of the polymer are independently selected from units having the general formula X-PEO-T wherein X is selected from H, C₁₋₄ alkyl, C₁₋₄ hydroxyalkyl and C₁₋₄ acyl.

20 Also preferred herein from the viewpoint of achieving optimum soil-release and clay-soil cleaning performance are soil release polymers having a molecular weight in the range from 1,000 to 4,900, preferably from 1,500 to 4,500, and an EO-T/PEO-T molar ratio of from 0.6 to 0.95, preferably from 0.65 to 0.85. The PEO molecular weight, on the other hand, is preferably from 1,000 to 2,000, more preferably from 1,200 to 1,800.

25 The molar ratio of EO-T to PEO:T units is determined herein by 270 MHz proton NMR, the ratio being directly derived from the relative peak areas of the C₆H₄CO₂CH₂ methylene resonances attributable to EO-T and PEO-T groups respectively. Molecular weight, on the other hand, is determined herein by measuring the specific viscosity of a solution of the polymer in chloroform at 0.5 g/dl concentration using an Ostwald No 100 viscometer, the number average molecular weight (M) being related to the specific viscosity (N_{sp}) and concentration (c) by the equation

$$M = 3.6236 \times 10^4 (N_{sp}/c)^{1.3852}$$

30 The compositions of the invention also contain from 0.1% to 20%, preferably from 0.5% to 15%, especially from 1% to 5% of a water-soluble quaternary ammonium surfactant. Preferred for use herein are quaternary ammonium surfactants having the general formula:



35 wherein R² is an alkyl, alkenyl or alkyl benzyl group having from 8 to 18 carbon atoms, preferably 10 to 14 carbon atoms in the alkyl chain; each R³ is selected from -CH₂CH₂- , -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂- , and mixtures thereof; each R⁴ is selected from C_{1-C4} alkyl, C_{1-C4} hydroxyalkyl, benzyl, ring structures formed by joining the two R⁴ groups,

40 -CH₂CHOHCHOHOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than 1,000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than 18; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

45 Preferred of the above are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when R⁵ is selected from the same groups as R⁴. The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate alkyl trimethylammonium salts, alkyl di(hydroxyethyl)methylammonium salts, alkyl hydroxyethyltrimethylammonium salts, and alkyloxypropyl trimethylammonium salts wherein alkyl is C_{8-C16}, preferably C_{10-C14}. Of the above, decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl trimethylammonium bromide and coconut trimethylammonium chloride and methylsulfate are particularly preferred.

50 Other useful cationic surfactants are disclosed in US-A 4 259 217.

55 Highly preferred water-soluble cationic surfactants herein have a critical micelle concentration (CMC) as measured for instance by surface tension or conductivity of at least 200 ppm, preferably at least 500 ppm at 30°C and in distilled water – see for instance Critical Micelle Concentrations of Aqueous Surfactant Systems, P. Mukerjee and K J Mysels NSRDS-NBS 36, (1971).

60 The compositions of the invention can take the form of a conventional main wash laundry detergent composition or of a laundry additive composition for use together with a separate main-wash detergent composition. In either instance, however, the compositions herein contain from 5% to about 25%, preferably from 5% to 25% by weight of anionic or nonionic surfactant. The compositions can also be complemented by other usual laundry detergent components such as detergency builders, bleaches etc.

65 Suitable synthetic anionic surfactants are water-soluble salts of C_{8-C22} alkyl benzene sulphonates, C_{8-C22} alkyl sulphates, C₁₀₋₁₈ alkyl polyethoxy ether sulphates, C₈₋₂₄ paraffin sulphonates, alpha-C₁₂₋₂₄ olefin sulphonates, alpha-sulphonated C_{6-C20} fatty acids and their esters, C_{10-C18} alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, especially those prepared

from coconut oil, C₈-C₁₂ alkyl phenol polyethoxy ether sulphates, 2-acyloxy C₉-C₂₃ alkane-1-sulphonate, and beta-alkyloxy C₈-C₂₀ alkane sulphonates.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from 8 to 22, especially from 10 to 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups).

Examples of this group of synthetic detergents are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C₈-18) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from 9 to 15, especially 11 to 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.-A-2,220,099 and U.S.-A-2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is 11.8 carbon atoms, abbreviated as C_{11.8} LAS, and C₁₂-C₁₅ methyl branched alkyl sulphates.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred.

Suitable fatty acid soaps herein can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkyldiammonium salts of higher fatty acids containing from 8 to 24, preferably from 10 to 22 and especially from 16 to 22 carbon atoms in the alkyl chain. Fatty acids in partially neutralized form are also suitable for use herein, especially in liquid compositions. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:5, preferably from 5:1 to 1:1, more preferably from 5:1 to 1.5:1. Especially preferred is a mixture of an alkyl benzene sulphonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulphate having from 10 to 20, preferably 12 to 18 carbon atoms in the alkyl radical or an ethoxy sulphate having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, having an alkali metal cation, preferably sodium.

Nonionic surfactants suitable herein are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range preferably from 9.5 to 13.5, more preferably from 10 to 12.5.

The nonionic surfactants for use herein include the condensation products of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols (RTm), Dobanols (RTm) and Neodols (RTm) which have about 25% 2-methyl branching (Lutensol (RTm) being a Trade Name of BASF, Dobanol (RTm) and Neodol (RTm) being Trade Names of Shell), or Synperonics (RTm), which are understood to have about 50% 2-methyl branching (Synperonic (RTm) is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants preferred for use herein include Dobanol (RTm) 45-4, Dobanol (RTm) 45-7, Dobanol (RTm) 91-6, Dobanol (RTm) 91-8, Dobanol (RTm) 23-6.5, and Synperonic (RTm) 6.

Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol (RTm) series having from 9 to 15 carbon atoms in the alkyl group and from 3 to 9 ethoxy residues per molecule.

Especially preferred nonionic surfactants for use herein are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₂-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

Suitable builder salts useful in the compositions of the invention can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. The level of these materials is generally from 15% to 90%, preferably from 20% to 60% by weight of the total laundry composition. Non-limiting examples of suitable water-soluble, inorganic alkaline builder salts include the alkali metal carbonates, borates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates.

Organic builder/chelating agents that can be incorporated include organic polycarboxylates and aminopolycarboxylates and their salts, organic phosphonate derivatives such as those disclosed in US-A 3

213 030, US-A 3 433 021, US-A 3 292 121 and US-A 2 599 807, and carboxylic acid builder salts such as those disclosed in US-A 3 308 067.

Preferred chelating agents include citric acid, nitrilotriacetic (NTA) and ethylenediamine tetra acetic acids (EDTA), hydroxyethylmethylenediaminetriacetic acid (HEEDTA), nitrilo(trimethylene phosphonic acid) (NTMP), ethylenediamine tetra(methylene phosphonic acid) (EDTMP) and diethylenetriamine penta(methylene phosphonic acid) (DETPMP) and salts thereof. Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA A 755 038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

As mentioned earlier, a valuable feature of the invention is the improved clay-soil detergency performance observed in compositions having a low or zero phosphate builder content. Accordingly, preferred compositions herein have a phosphorus content of less than 5%, preferably less than 2% by weight. In compositions of this type, the builder preferably belongs to the aluminosilicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation $\text{Na}_z(\text{AlO}_2)_z(\text{SiO}_2)_y\text{xH}_2\text{O}$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5 and x is an integer from 15 to 264. Compositions incorporating builder salts of this type form the subject of GB-A 1 429 143, DE-A 2 433 485, and DE-A 2 525 778.

The laundry compositions herein can be supplemented by all manner of detergent and laundering components.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate is preferably from 3% to 15% by weight of the total composition. Suitable silicate solids have a molar ratio of $\text{SiO}_2/\text{alkali metal}_2\text{O}$ in the range from 0.5 to 3.3, more preferably from 1.0 to 2.0.

The laundry compositions herein can also contain bleaching components. In general, the bleach is selected from inorganic peroxy salts, hydrogen peroxide, hydrogen peroxide adducts, and organic peroxy acids and salts thereof. Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persilicate, urea-hydrogen peroxide addition products and the clathrate $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot \text{NaCl}$. Suitable organic bleaches include peroxyalauric acid, peroxyoctanoic acid, peroxynonanoic acid, peroxydecanoic acid, diperoxydodecanoic acid, diperoxyazelaic acid, mono- and diperoxyphthalic acid and mono- and diperoxyisophthalic acid and salts (especially the magnesium salts) thereof. The bleaching agent is generally present at a level of from 5% to 35%, preferably from 10% to 25% by weight of total laundry composition. Peroxyacid bleach precursors suitable herein are disclosed in UK-A-2040983, highly preferred being peracetic acid bleach precursors such as tetraacetylethylene diamine, tetraacetylmethylenediamine, tetraacetylhexylenediamine, sodium p-acetoxybenzene sulphonate, tetraacetylglycoluril, pentaacetylglucose, octaacetylactose, methyl O-acetoxy benzoate, sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate, sodium 3,5,5-trimethylhexanoyloxybenzoate, sodium 2-ethylhexanoyloxybenzenesulfonate, sodium nonanoyloxybenzenesulfonate and sodium octanoyloxybenzenesulfonate. In laundry detergent compositions, the level of bleach precursor is generally from 0.5% to 10%, preferably from 1% to 6% by weight of the total composition. In additive compositions, however, the bleach precursor is preferably added in a level of from 1% to 50%, preferably from 5% to 35% by weight thereof.

Other optional components of the compositions herein include suds suppressors, enzymes, fluorescers, photoactivators, soil suspending agents, anti-caking agents, pigments, perfumes, fabric conditioning agents etc.

Suds suppressors are represented by materials of the silicone, wax, vegetable and hydrocarbon oil and phosphate ester varieties. Suitable silicone suds controlling agents include polydimethylsiloxanes having a molecular weight in the range from 200 to 200,000 and a kinematic viscosity in the range from 20 to 2,000,000 mm²/s, preferably from 3000 to 30,000 mm²/s, and mixtures of siloxanes and hydrophobic silanated (preferably trimethylsilanated) silica having a particle size in the range from 10 nm to 20 nm and a specific surface area above 50 m²/g. Suitable waxes include microcrystalline waxes having a melting point in the range from 65°C to 100°C, a molecular weight in the range from 4000–1000, and a penetration value of at least 6, measured at 77°C by ASTM-D1321, and also paraffin waxes, synthetic waxes and natural waxes. Suitable phosphate esters include mono- and/or di-C₁₆–C₂₂ alkyl or alkenyl phosphate esters, and the corresponding mono- and/or dialkyl or alkenyl ether phosphates containing up to 6 ethoxy groups per molecule.

Enzymes suitable for use herein include those discussed in US-A 3 519 570 and US-A 3 533 139. Suitable fluorescers include Blankophor (RTm) MBBH (Bayer AG) and Tinopal (RTm) CBS-X and EMS (Ciba Geigy). Photoactivators are discussed in EP-A 57 088, highly preferred materials being zinc phthalocyanine, tri- and tetra-sulfonates. Suitable fabric conditioning agents include smectite-type clays as disclosed in GB-A 1 400 898 and di-C₁₂–C₂₄ alkyl or alkenyl amines and ammonium salts.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-

1,596,756. Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least 10 mole percent, preferably at least 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

The laundry detergent and additive compositions of the invention can be formulated, packaged and retailed in conventional granular, powdery or liquid form but preferably, the composition is formulated as part of a laundry product comprising the composition in water-releasable combination with a water-insoluble substrate or a single- or multi-compartment sachet. Laundry products of this kind are valuable herein from the viewpoint of providing a slow and sustained release of the soil-removal polymer into the laundry solution, a factor which appears to be beneficial for achieving optimum soil-release and single-cycle cleaning advantages.

Laundry products preferred for use herein comprise a substrate or sachet formed from a flexible, water-insoluble sheet-like material. The sheet-like material may be made of paper, woven or non-woven fabrics or the like.

The basis weight of the water-insoluble sheet is preferably from 10 to 70 grams/sq metre, more preferably from 20 to 50 grams/sq metre. Preferred materials for use herein are apertured nonwoven fabrics which can generally be defined as adhesively or thermo-bonded fibrous or filamentous products, having a web or carded fibre structure (where the fibre strength is suitable to allow carding) or comprising fibrous mats, in which the fibres of filaments are distributed haphazardly or in random array (i.e. an array of fibres in a carded web wherein partial orientation of the fibres is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibres or filaments can be natural (e.g. wool, silk, wood pulp, jute, hemp, cotton, linen, sisal, or ramie), synthetic (e.g. rayon, cellulose, ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters) or mixtures of any of the above.

Generally, non-woven cloths can be made by air or water laying processes in which the fibres or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fibre-laden air or water is passed. The deposited fibres or filaments are then adhesively or thermo-bonded together, dried cured and otherwise treated as desired to form the non-woven cloth. Non-woven cloths which are spin-bonded, spin-laced or melt-blown are also suitable however.

Preferably, the non-woven cloth is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant such as sodium oleate. The non-woven cloth preferably also has a content of a polyolefin such as polypropylene to allow for heat sealing to the poly(ethylene oxide) film. Preferably the fibres are from 4 to 50 mm, especially from 8 mm to 20 mm, in length and are from 1.1 to 5.6 dtex (1 to 5 denier) (dtex is an internationally recognised unit in yarn measure, corresponding to the weight in decigrams of a 1000 meter length of yarn).

Preferably the fibres are at least partially orientated haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. In highly preferred embodiments, the cloth comprises from 75% to 88%, especially from 78% to 84% fibre and from 12% to 25%, especially from 16% to 22% hydrophobic binder-resin polymer by weight and has a basis weight of from 10 to 70, preferably from 20 to 50 g/m². Suitable hydrophobic binder-resins are ethylacrylate resins such as Primal (RTm) HA24, Rhoplex (RTm) HA8 and HA16 (Rohm and Haas, Inc) and mixtures thereof.

The substrate apertures, which extend between opposite surfaces of the substrate, are normally in a pattern and are formed during lay-down of the fibres to produce the substrate. Exemplary apertured non-woven substrates are disclosed in US Patent Nos. 3 741 724, 3 930 086 and 3 750 237.

An example of an apertured non-woven substrate suitable herein is a polypropylene-containing regenerated cellulose sheet of 1.7 dtex (1.5 denier) fibres bonded with Rhoplex (RTm) HA 8 binder (fibre:binder ratio of 77:23) having a basis weight of 35 g/m² and 17 apertures/cm². The apertures are generally elliptical in shape and are in side-by-side arrangement. The apertures have a width of 0.9 mm and a length of 2.5 mm measured in a relaxed condition. Another highly preferred substrate based 1.7 on dtex (1.5 denier) regenerated cellulose fibres with Rhoplex HA8 binder has a fibre:binder ratio of 82:18, a basis weight of 35 g/m², and 22 apertures/cm². In this example, the apertures are generally square-shaped with a width of 1.1 mm. The apertures are again disposed in side-by-side arrangement.

In the substrate embodiments of the invention, the laundry composition is coated on or impregnated into the substrate at a weight ratio of composition : substrate of at least 3:1, preferably at least 5:1. In these embodiments, the laundry composition preferably contains at least 5%, more preferably at least 15% by weight of composition of water-soluble or water-dispersible organic binding agent. Preferably, the binding agent is selected from polyethylene glycols of molecular weight greater than 1,000, more preferably greater than 4,000, C₁₂-C₁₈ fatty acids and esters and amides thereof, polyvinyl pyrrolidone of molecular weight in the range from 40,000 to 700,000, and C₁₄-C₂₄ fatty alcohols ethoxylated with from 14 to 100 moles of ethylene oxide.

The laundry compositions of the invention in granular or powder form are preferably made by spray-drying an aqueous slurry comprising anionic surfactant and detergency builder to a density of at least 0.3g/cc, spraying-on nonionic surfactant, where present, and optionally comminuting the spray-dried

granules in for example a Patterson-Kelley twin shell blender to a bulk density of at least 0.5g/cc. The aqueous slurry for spray drying preferably comprises from 30% to 60% water and from 40% to 70% of the detergency builder; it is heated to a temperature of from 60°C to 90°C and spray dried in a current of air having an inlet temperature of from 200°C to 400°C, preferably from 275°C to 350°C, and an outlet temperature of from 95°C to 125°C, preferably from 100°C to 115°C. The weight average particle size of the spray dried granules is from 0.15 to 3mm, preferably from 0.5 mm to 1.4 mm. After comminution, the weight average particle size is from 0.1 to 0.5 mm, preferably from 0.15 to 0.4 mm.

In the Examples, the abbreviations used have the following designation:

LAS : Linear C₁₂ alkyl benzene sulphonate

TAS : Tallow alkyl sulphate

C_{14/15}AS : Sodium C₁₄-C₁₅ alkyl sulphate

TAE_n : Hardened tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol

C₁₄TMAB : C₁₄ alkyl trimethyl ammonium bromide

Dobanol (RTm) 45-E-7 : A C₁₄-C₁₅ primary alcohol condensed with 7 moles of ethylene oxide, marketed by Shell

Clay : Sodium montmorillonite

INOBS : Sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate

TAED : Tetraacetylenediamine

Silicone/silica : 85:15 mixture of polydimethylsiloxane and silanated silica prilled with STPP and TAE₈₀

Enzyme : Savinase (RTm) prills

STPP : Sodium tripolyphosphate

Zeolite : Zeolite 4A

Polymer : Terephthalate Soil release polymer; EO-T/PEO:T =0.6; Molecular weight = 3,800

Gantrez (RTm) AN119: Maleic anhydride/vinyl methyl ether copolymer mol. wt about 240,000

Metasilicate : Sodium metasilicate

Na₂CO₃ : Sodium carbonate

Silicate : Sodium silicate (SiO₂:Na₂O = 1.6:1)

Perborate : Anhydrous sodium perborate bleach of empirical formula NaBO₂H₂O₂

Percarbonate : Sodium percarbonate

MA/AA : Maleic acid/acrylic acid copolymer, 1:3 mole ratio, m.wt. 70,000

EDTA : Sodiummethylenediaminetetraacetate

Brightener : Tinopal (RTM) CBS-X

EDTMP : Ethylenediamine tetra(methylene phosphonic acid), marketed by under the Trade name

Dequest (RTm) 2041

Substrate : Non-woven fabric formed of 100% unbleached crimped rayon fibres of 1.7 dtex (1.5 denier) bonded with 18% polyacrylate binder; basis weight 35 g/m²; 22 square-shaped apertures/cm²; side dimension 1.1 mm

EXAMPLES 1 TO 5

Laundry additive products according to the invention are prepared as follows. For each product, the components of the laundry additive composition are mixed at a temperature of 65°C and passed through a Fryma (RTm) Colloid Mill, Model MK95-R/MZ 80R (made by M.M. Process Equipment Ltd of M.M. House, Frogmore Road, Hemel Hempstead, Hertfordshire, United Kingdom) in which the grinding faces are set to a separation of 180 µm. The melt is then fed through a pair of counterrotating rolls heated to 76°C and having a nip setting of 250 µm and is transferred to substrate moving counter to one of the rollers by wiping. The coated substrate is finally passed between a pair of static plates having a spacing of 180 µm, air-cooled, and cut into sheets of size 35 x23 cm.

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		<u>EXAMPLES</u>				
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
5	LAS	-	3	-	-	5
	C₁₂/14 AS	5	3	6	-	3
	TAE₂₅	-	3	-	-	-
10	C₁₄ TMAB_(RTM)	2	3	4	2	1
	Dobanol/ 45-E-7	5	3	5	5	5
	PEG 8000	5	5	7	4	7
15	TAED	5	-	-	5	-
	INOBS	-	3	-	-	3
20	Silicone/Silica_(RTM)	0.3	0.2	0.2	0.2	0.3
	Gantrez/AN119	0.3	-	-	0.5	-
	Perborate	-	-	5	-	-
25	EDTA	-	-	-	-	-
	Polymer	1	0.5	2	1	2
	Brightener	-	0.3	0.1	0.1	0.2
30	EDTMP	-	-	1.5	0.5	-
	Moisture	0.8	0.5	0.6	0.2	0.5
	Substrate	2.6	2.6	2.6	2.6	2.6

When used as laundry additive products together with a main wash laundry detergent composition, the above products provide excellent soil release performance without detriment to clay-soil detergency and anti-redeposition performance.

EXAMPLES VI TO X

Five laundry products are prepared as follows:

A base powder composition is first, prepared by mixing all components except Dobanol (RTm) 45E7, bleach, bleach activator, enzyme, suds suppressor, phosphate and carbonate in a crutcher as an aqueous slurry at a temperature of 55°C and containing 35% water. The slurry is then spray dried at a gas inlet temperature of 330°C to form base powder granules and the granules are comminuted in a Patterson-Kelley twin shell blender. The bleach activator where present, is then admixed with TAE₂₅ as binder and extruded in the form of elongate particles through a radial extruder as described in EP-A 0 062 523. The bleach activator noodles, bleach, enzyme, suds suppressor, phosphate and carbonate are then dry-mixed with the base powder composition and finally Dobanol (RTm) 45E7 is sprayed into the final mixture. Each composition had a bulk density of about 0.7 g/cc.

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		VI	VII	VIII	IX	X
5	LAS	5	8	8	3	4
TAS	-	-	3	-	4	
10	C _{14/15} AS	5	8	-	1	-
TAE ₂₅	0.5	0.3	0.5	0.2	0.8	
15	C ₁₄ TMAB (RTA)	2	3	1	1	2
Dobanol _{45-E-7}	2	2	4	10	4	
Clay	-	6	-	-	4	
INOBS	-	2	4	-	-	
TAED	3	-	0.5	-	2	
20	Polymer	2	3	1	4	2
Silicone/Silica	0.2	0.2	0.4	0.8	0.4	
Enzyme	0.5	0.6	0.7	0.8	0.5	
25	STPP	6	-	18	-	2
Zeolite	12	18	6	22	20	
30	Metasilicate	-	-	-	-	-
Na ₂ CO ₃	5	-	8	-	-	
Silicate	5	6	10	6	6	
35	Perborate	10	-	14	-	-
Percarbonate	-	-	-	-	20	
MA/AA	4	3	2	2	4	
40	EDTA	0.5	0.5	0.5	0.5	0.5
Brightener	0.2	0.2	0.2	0.2	0.2	
EDTMP	0.2	0.1	0.2	0.3	0.2	
45	Sulphate, moisture	<u>To 100</u>				

A twin-compartment sachet is made from a non-woven fabric formed of 100% unbleached crimped rayon fibres of 1.7 dtex (1.5 denier) bonded with 18% polyacrylate builder, the non-woven fabric having a basis weight of 35 g/m². The sachet is made from a sheet of the fabric measuring 120 mm x 80 mm by folding midway along the long dimension, sealing along the two opposing free edges with sodium silicate solution and along a longitudinal seam parallel to and half-way between the two opposing edges, filling the two compartments with 120cc each of detergent composition VI and then sealing along the open edge of the sachet. The procedure is then replicated four times using composition VII to X respectively.

When used as main-wash laundry detergent products, the above examples provide excellent soil-release performance without detriment to clay-soil detergency and anti-redeposition performance.

Claims

- 60 1. A laundry detergent or detergent additive composition comprising:
 - (a) from 0.1% to 25% by weight of a soil-release polymer comprising ethyleneoxy terephthalate (EO-T) units and polyethyleneoxy terephthalate (PEO-T) units at a molar ratio (EO-T/PEO-T) of from 0.6 to 0.95, the PEO-T units containing polyethylene oxide (PEO) linking units having a molecular weight of from 300 to about 3000, the molecular weight of the polymer being in the range from 900 to 9,000;
 - (b) from 0.1% to 20% of a water-soluble quaternary ammonium surfactant; and

(c) from 5% to 75% of anionic or nonionic surfactant, wherein the nonionic surfactant comprises an ethylene oxide condensation product selected from C₈-C₂₄ primary or secondary aliphatic alcohols having from 2 to 9 moles of ethylene oxide per mole of alcohol.

2. A composition according to Claim 1 wherein the soil-release polymer comprises at least 10%, preferably at least 20% thereof (molar basis) of components wherein both chain terminating units of the polymer are independently selected from units having the general formula X-PEO-T wherein X is selected from H, C₁₋₄ alkyl, C₁₋₄ hydroxyalkyl and C₁₋₄ acyl.

3. A composition according to Claim 1 or 2 wherein the soil release polymer has a molecular weight in the range from 1000 to 4900, preferably from 1500 to 4500.

4. A composition according to any of Claims 1 or 3 wherein the soil-release polymer has an EO-T/PEO-T molar ratio of from 0.65 to 0.85 and a PEO molecular weight of from 1000 to 2000, preferably from 1200 to 1800.

5. A composition according to any of Claims 1 to 4 wherein the water-soluble quaternary ammonium surfactant has the general formula:



wherein R² is an alkyl, alkenyl or alkyl benzyl group having from 8 to 18 carbon atoms, preferably 10 to 14 carbon atoms in the alkyl chain; each R³ is selected from -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from C_{1-C4} alkyl, C_{1-C4} hydroxyalkyl, benzyl, ring structures formed by joining the two R⁴ groups,

20 -CH₂CHOHCHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than 18; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

6. A composition according to any of Claims 1 to 5 having a phosphorus content of less than 5%, preferably less than 2%.

7. A composition according to Claim 6 comprising from 5% to 50% of a water-insoluble aluminosilicate ion-exchange material.

8. A laundry product comprising a laundry detergent composition according to any of Claims 1 to 7 in water-releasable combination with a water-insoluble substrate or a single- or multicompartment sachet.

Patentansprüche

1. Wäschewaschdetergens- oder Dergenszusatzzusammensetzung, umfassend:

a) von 0,1 Gew.-% bis 25 Gew.-% eines Schmutzlösepolymer, umfassend Ethylenoxyterephthalat (EO-T) -Einheiten und Polyethylenoxyterephthalat (PEO-T) -Einheiten in einem Molverhältnis von (EO-T/PEO-T) von 0,6 bis 0,95, wobei die PEO-T-Einheiten verknüpfende Polyethylenoxid (PEO) -Einheiten mit einem Molekulargewicht des Polymers im Bereich von 900 bis 9000 liegt;

b) von 0,1% bis 20% eines wasserlöslichen quaternären Ammonium-grenzflächenaktiven Mittels; und

c) von 5% bis 75% an anionischem oder nichtionischem grenzflächenaktivem Mittel, worin das nichtionische grenzflächenaktive Mittel ein Ethylenoxidkondensationsprodukt umfaßt, welches aus primären oder sekundären, aliphatischen C₈-C₂₄-Alkoholen mit 2 bis 9 Mol Ethylenoxid je Mol Alkohol ausgewählt ist.

2. Zusammensetzung nach Anspruch 1, worin das Schmutzlösepolymer mindestens 10%, vorzugsweise mindestens 20% hiervon (auf einer molaren Basis) an Komponenten enthält, worin beide die Kette beschließenden Einheiten des Polymers unabhängig voneinander von Einheiten mit der allgemeinen Formel X-PEO-T ausgewählt sind, worin X aus H, C₁₋₄-Alkyl, C₁₋₄-Hydroxyalkyl und C₁₋₄-Acyl ausgewählt ist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin das Schmutzlösepolymer ein Molekulargewicht im Bereich von 1000 bis 4900, vorzugsweise von 1500 bis 4500 besitzt.

4. Zusammensetzung nach einem der Ansprüche 1 oder 3, worin das Schmutzlösepolymer ein molares Verhältnis von EO/PEO-T von 0,65 bis 0,85 und ein PEO-Molekulargewicht von 1000 bis 2000, vorzugsweise von 1200 bis 1800 besitzt.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin das wasserlösliche quaternäre Ammonium-grenzflächenaktive Mittel die allgemeine Formel:



besitzt, worin R² eine Alkyl-, Alkenyl- oder Alkylbenzylgruppe mit 8 bis 18 Kohlenstoffatomen, vorzugsweise 10 bis 14 Kohlenstoffatomen in der Alkylkette darstellt; jedes R³ unter -CH₂CH₂-,

-CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, und Gemischen hiervon ausgewählt ist; jedes R⁴ unter C_{1-C4}-Alkyl, C_{1-C4}-Hydroxyalkyl, Benzyl, Ringstrukturen welche durch Verbinden der beiden R⁴-Gruppen ausgebildet werden, -CH₂CHOHCHOHCOR⁶CHOHCH₂OH, worin R⁶ irgendeine Hexose oder ein Hexosepolymer mit einem Molekulargewicht von weniger als 1000 ist, und Wasserstoff, wenn y nicht den Wert 0 besitzt, ausgewählt ist; R⁵ die gleiche Bedeutung wie R⁴ besitzt oder eine Alkylkette darstellt, wobei die Gesamtzahl an Kohlenstoffatomen von R² plus R⁵ nicht mehr als 18 beträgt; jedes y von 0 bis 10 beträgt, und die Summe der y-Werte von 0 bis 15 ist; und X jedes beliebige annehmbare Anion ist.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, welche einen Phosphorgehalt von weniger als 5%, vorzugsweise von weniger als 2% besitzt.
7. Zusammensetzung nach Anspruch 6, welche von 5% bis 50% eines wasserunlöslichen Aluminiumsilicationenaustauschmaterials umfaßt.
- 5 8. Wäschewaschprodukt, umfassend eine Wäschewaschdetergenszusammensetzung nach einem der Ansprüche 1 bis 7 in Wasser-freisetzbarer Kombination mit einem wasserunlöslichen Substrat oder einem Säckchen mit einer oder mehreren Kammern.

Revendications

- 10 1. Composition détergente de blanchissage ou additive pour détergent, comprenant:
- (a) de 0,1% à 25% en poids d'un polymère anti-salissures comprenant des motifs d'éthylèneoxytérphthalate (EO-T) et des motifs de polyéthylèneoxytérphthalate (PEO-T) dans un rapport molaire (EO-T/PEO-T) de 0,6 à 0,95, les motifs de PEO-T contenant des motifs de liaison de poly(oxyde d'éthylène) PEO ayant une masse moléculaire de 300 à 3000, la masse moléculaire du polymère étant dans l'intervalle de 900 à 9000;
- (b) de 0,1% à 20% d'un tensioactif ammonium quaternaire hydrosoluble; et
- (c) de 5% à 75% de tensioactif anionique ou non ionique, dans lequel le tensioactif non ionique comprend un produit de condensation d'oxyde d'éthylène choisi parmi les alcools aliphatiques primaires ou secondaires en C₈-C₂₄ comportant de 2 à 9 moles d'oxyde d'éthylène par mole d'alcool.
- 20 2. Composition selon la revendication 1, dans laquelle le polymère anti-salissures comprend au moins 10%, de préférence au moins 20%, en pourcentage molaire, de constituants dans lesquels les deux motifs de terminaison des chaînes du polymère sont choisis indépendamment parmi les motifs répondant à la formule générale X-PEO-T, dans laquelle X est choisi parmi H, les groupes alkyle en C₁-C₄, hydroxylkyle en C₁-C₄ et acyle en C₁-C₄.
- 25 3. Composition selon la revendication 1 ou 2, dans laquelle le polymère anti-salissures a une masse moléculaire dans l'intervalle de 1000 à 4900, de préférence de 1500 à 4500.
4. Composition selon l'une quelconque des revendications 1 ou 3, dans laquelle le polymère anti-salissures a un rapport molaire EO-T/PEO-T de 0,65 à 0,85 et une masse moléculaire de PEO de 1000 à 2000, de préférence de 1200 à 1800.
- 30 5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le tensioactif ammonium quaternaire hydrosoluble répond à la formule générale:
 $[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N^+X^-$
- 35 dans laquelle R² est un groupe alkyle, alcényle ou alkylbenzyle comportant de 8 à 18 atomes de carbone, de préférence de 10 à 14 atomes de carbone, dans la chaîne alkyle; chaque R³ est choisi parmi -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂- et leurs mélanges; chaque R⁴ est choisi parmi les groupes alkyle en C₁-C₄, hydroxylkyle en C₁-C₄, benzyle, les structures cycliques formées par la liaison des deux groupes R⁴, -CH₂CHOHCHOHCOR⁶CHOHCH₂OH, dans lequel R⁶ est un hexose ou polymère d'hexose quelconque ayant une masse moléculaire inférieure à 1000, et un hydrogène lorsque y n'est pas nul; R⁵ est identique à R⁴ ou est une chaîne alkyle dans laquelle le nombre total d'atomes de carbone de R² et de R⁵ ne dépasse pas 18; chaque y a une valeur de 0 à 10 et la somme des y a une valeur de 0 à 15; et X est n'importe quel anion compatible.
- 40 6. Composition selon l'une quelconque des revendications 1 à 5 ayant une teneur en phosphore inférieure à 5%, de préférence inférieure à 2%.
- 45 7. Composition selon la revendication 6, comprenant de 5% à 50% d'une substance échangeuse d'ions de type aluminosilicate, insoluble dans l'eau.
8. Produit de blanchissage comprenant une composition détergente de blanchissage selon l'une quelconque des revendications 1 à 7 en combinaison libérable à l'eau avec un substrat insoluble dans l'eau ou un sachet à un seul compartiment ou à plusieurs compartiments.

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